Structural Studies of Metal Complexes with Sulphur-containing Bidentate Ligands. Part 2.† Evidence for a Metal–Metal Bond from the Molecular Structures of Bis(phenyldithioacetato)-nickel(II) and -palladium(II)

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The molecular structures of the title complexes consist of binuclear bridged units of composition $[M_2(S_2CCH_2Ph)_4]$ in which each metal atom is co-ordinated to four sulphur and to the other metal atoms in a square-pyramidal geometry. Other evidence for a metal–metal bond is obtained from a comparison of the metal–sulphur distances and those in nickel and palladium square-planar complexes with comparable –S– and –M– angles. The crystal structures have been solved from *X*-ray data by the heavy-atom technique and refined by anisotropic least squares to final *R* values of 0.06 (Ni) and 0.05 (Pd). The two complexes are isostructural and isomorphous, both crystallizing in space group *Iba*2, with $Z = 4$ in unit cells of dimensions $a = 9.232(3)$, $b = 29.420(7)$, $c = 12.097(3)$ Å, and $a = 9.334(5)$, $b = 29.592(5)$, $c = 12.023(5)$ Å, respectively.

DITHIOCARBOXYLATO-COMPLEXES are often rather different from other d^8–d^{10} complexes of bivalent transition metals with bidentate dithio-ligands, and these differences clearly depend on the characteristics of the RCS_2^- group.[1] Thus, in nickel and palladium dithiobenzoato-complexes four-membered rings are formed,[2] while in the corresponding phenyldithioacetates $[M_2(S_2CCH_2Ph)_4]$ (M = Ni or Pd) and nickel dithioacetate, $[Ni_2(S_2CMe)_4]$,‡ the dithio-ligands act as bridging groups between two metal atoms with the formation of binuclear units. In the present paper we compare the structure of $[Ni_2(S_2CCH_2Ph)_4]$, already briefly reported[3] and spectroscopically studied by Furlani *et al.*,[4] and that of $[Pd_2(S_2CCH_2Ph)_4]$ solved in these laboratories.

EXPERIMENTAL

The title complexes were prepared following the methods of Furlani *et al.*[4] Their crystals were stable in the air and in the *X*-ray beam. Unit-cell dimensions, measured at room temperature, were determined from zero-layer Weissenberg films taken about the *a* and *c* axes for $[Ni_2(S_2CCH_2Ph)_4]$, and from a zero-layer Weissenberg film taken about the *c* axis, and a precession photograph taken about the *a* axis, for $[Pd_2(S_2CCH_2Ph)_4]$. Reflections mainly from Cu-$K_{\alpha 1}$ radiation were used (λ 1.540 6 Å).

Crystal Data.—Bis(phenyldithioacetato)nickel(II). $C_{32}H_{28}Ni_2S_8$, $M = 786.512$, red-brown orthorhombic prisms, $a = 9.232(3)$, $b = 29.420(7)$, $c = 12.097(3)$ Å, $U = 3\,286$ Å^3, $D_m = 1.59$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.591$ g cm^{-3}, $F(000) = 1\,580.5$, $\mu(\text{Cu-}K_\alpha) = 61.57$ cm^{-1}. Space group *Iba*2 from systematic absences and the structure determination. The intensities of 2 065 reflections above film background were collected from equi-inclination Weissenberg layers 0—6*kl* and *hk*0—7 to give a set of 1 335 independent reflections (*ca.* 60% of those possible with Cu-K_α radiation). Intensity data were corrected for Lorentz and polarization effects, and for spot extension. Absorption and extinction corrections were not applied.

Bis(phenyldithioacetato)palladium(II). $C_{32}H_{28}Pd_2S_8$, $M = 881.892$, dark brown orthorhombic prisms, $a = 9.334(5)$, $b = 29.592(5)$, $c = 12.023(5)$ Å, $U = 3\,321$ Å^3, $D_m = 1.75$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.754$ g cm^{-3}, $F(000) = 1\,733.08$, $\mu(\text{Cu-}K_\alpha) = 136$ cm^{-1}. Space group *Iba*2. Diffraction data were collected from a single-crystal prism of average radius 0.088 cm mounted on a glass with the *c* axis

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† Part 1 is ref. 2.

‡ The molecular structure of $[Ni_2(S_2CMe)_4]$ is very similar to that of $[Ni_2(S_2CCH_2Ph)_4]$. Its refinement is in progress and it will not be discussed here.

[1] M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J.C.S. Dalton*, 1972, 2515.

[2] Part 1, M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J.C.S. Dalton*, 1975, 2250.

[3] M. Bonamico, G. Dessy, and V. Fares, *Chem. Comm.*, 1969, 1106.

[4] C. Furlani, O. Piovesana, and A. A. G. Tomlinson, *J.C.S. Dalton*, 1972, 212.

parallel to the fibre axis. Intensities were measured using a STOE automatic Weissenberg diffractometer. Nickel-filtered Cu-K_α radiation was monochromatized by a plane graphite crystal. Two sets of data were collected from eight layers, $hk0$—7: the first in a θ—2θ scan ($14 \leqslant 2\theta \leqslant 140°$); the second, for low-angle reflections, in an ω scan. The background for each reflection was determined from two stationary-crystal–stationary-counter measurements at both the beginning and the end of the scan. The overall stability of the system was checked by monitoring a single reference reflection for each layer. Corrections were made for background, Lorentz, and polarization effects, and for absorption. No extinction correction was applied. A total of 1 283 independent reflections (58%) was considered significant (*i.e.* those having $I > 3C^{1/2}$, where C is the integrated intensity not corrected for background).

TABLE 1

Co-ordinates ($\times$ 10^4), with standard deviations in parentheses, for the nickel complex

	x/a	y/b	z/c
Ni(1)	0	0	0
Ni(2)	0	0	2 109(2)
S(1,1)	1 886(3)	462(1)	−83(3)
S(1,2)	−1 471(3)	590(1)	−108(3)
S(2,1)	2 352(3)	128(1)	2 232(3)
S(2,2)	−389(3)	747(1)	2 199(3)
C(1)	2 855(12)	406(3)	1 044(12)
C(2)	−1 211(12)	915(4)	990(12)
C(1,1)	4 325(14)	637(4)	1 089(14)
C(2,1)	−1 749(14)	1 397(4)	952(13)
C(1,2)	4 412(12)	1 014(4)	1 942(10)
C(1,3)	3 499(16)	1 382(5)	1 923(13)
C(1,4)	3 638(20)	1 732(6)	2 732(17)
C(1,5)	4 696(17)	1 708(5)	3 504(16)
C(1,6)	5 640(16)	1 345(5)	3 542(13)
C(1,7)	5 478(15)	995(4)	2 772(12)
C(2,2)	−556(13)	1 726(4)	668(11)
C(2,3)	−90(17)	2 067(5)	1 390(14)
C(2,4)	979(19)	2 370(5)	1 119(17)
C(2,5)	1 698(19)	2 332(5)	124(16)
C(2,6)	1 334(21)	1 990(6)	−601(16)
C(2,7)	210(16)	1 699(5)	−335(14)
H(1,1)	5 133	379	1 307
H(1,2)	4 563	775	284
H(2,1)	−2 166	1 488	1 760
H(2,2)	−2 572	1 427	329
H(1,3)	2 666	1 403	1 288
H(1,4)	2 894	2 023	2 725
H(1,5)	4 789	1 978	4 111
H(1,6)	6 523	1 334	4 155
H(1,7)	6 166	697	2 825
H(2,3)	−613	2 090	2 201
H(2,4)	1 224	2 639	1 695
H(2,5)	2 605	2 565	−65
H(2,6)	1 876	1 962	−1 392
H(2,7)	−87	1 435	−920

For both structures, independent layer scales were refined during the isotropic phase of structure refinement.

Calculations.—Calculations were made on the IBM 7040 and UNIVAC 1108 computers at Rome University using the system of programs of Laboratorio di Strutturistica Chimica del C.N.R. Neutral atomic-scattering factors were taken from ref. 5, and corrections for the anomalous dispersion of nickel, palladium, and sulphur from ref. 6.

Determination and Refinement of the Structures.—Since $Z = 4$, the dimeric molecule must lie on a two-fold axis, passing through the two metal atoms. The Z co-ordinates of the metal atoms and the approximate positions of the sulphur atoms were found from an unsharpened three-dimensional Patterson function. The other non-hydrogen atoms were obtained from subsequent Fourier syntheses. The positions and isotropic thermal parameters of the atoms were refined by using the block-diagonal approximation. At this stage R was 0.09 for the nickel and 0.06 for the palladium complex.

Hydrogen atoms were included at calculated positions (C–H 1.00 Å), with the average isotropic temperature factor of the phenyl groups (B 4.5 Å^2 for the nickel complex and 5.00 Å^2 for the palladium complex). The refinement was continued for non-hydrogen atoms using anisotropic thermal parameters for all the atoms, apart from the carbon atoms of the phenyl rings which retained the isotropic temperature factors. Convergence was achieved for both structures after three cycles of refinement. The weighting scheme $w = (a + bF_o + cF_o^2)^{-1}$ was used throughout the refinements, where $a = 5.00$, $b = 1.00$, and $c = 0.002$ for the nickel and $a = 9.00$, $b = 1.00$, and $c = 0.002$ for the palladium complex. The final R values were 0.059 (Ni) and 0.053 (Pd).

TABLE 2

Co-ordinates ($\times$ 10^4), with standard deviations in parentheses, for the palladium complex

	x/a	y/b	z/c
Pd(1)	0	0	0
Pd(2)	0	0	2 258(2)
S(1,1)	2 013(3)	462(1)	−20(5)
S(1,2)	−1 468(4)	638(1)	−46(5)
S(2,1)	2 439(3)	151(1)	2 349(6)
S(2,2)	−441(3)	780(1)	2 313(5)
C(1)	2 904(13)	417(4)	1 181(17)
C(2)	−1 214(12)	931(4)	1 134(18)
C(1,1)	4 371(12)	649(4)	1 196(18)
C(2,1)	−1 720(14)	1 428(4)	1 108(18)
C(1,2)	4 481(13)	1 024(4)	2 047(14)
C(1,3)	3 546(13)	1 378(6)	2 061(19)
C(1,4)	3 638(17)	1 717(7)	2 815(20)
C(1,5)	4 699(19)	1 714(6)	3 634(27)
C(1,6)	5 658(17)	1 347(5)	3 643(19)
C(1,7)	5 509(16)	1 002(5)	2 872(17)
C(2,2)	−495(15)	1 742(5)	792(14)
C(2,3)	−93(19)	2 082(8)	1 553(20)
C(2,4)	1 042(21)	2 386(6)	1 254(21)
C(2,5)	1 747(19)	2 342(6)	308(19)
C(2,6)	1 367(20)	2 006(6)	−448(19)
C(2,7)	254(17)	1 720(6)	−217(19)
H(1,1)	5 127	417	1 368
H(1,2)	4 556	780	443
H(2,1)	−2 086	1 513	1 861
H(2,2)	−2 507	1 459	549
H(1,3)	2 764	1 388	1 494
H(1,4)	2 939	1 973	2 785
H(1,5)	4 774	1 963	4 194
H(1,6)	6 446	1 336	4 205
H(1,7)	6 157	733	2 913
H(2,3)	−589	2 111	2 286
H(2,4)	1 304	2 636	1 773
H(2,5)	2 559	2 551	133
H(2,6)	1 909	1 974	−1 161
H(2,7)	−33	1 490	−783

Tables 1 and 2 give the positional parameters of the atoms and their standard deviations, within the chemical units. Observed and calculated structure factors, based on the final atomic parameters, and thermal parameters are listed in Supplementary Publication No. SUP 22114 (11 pp.).* Bond distances and angles with their standard deviations are listed in Tables 3 and 4.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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DISCUSSION

Nickel and palladium phenyldithioacetates are isostructural, the small differences found deriving from the increase in the covalent radius from 1.15 (Ni) to 1.28 Å (Pd). Overall views of the structures are shown in Figures 1 and 2. They consist of binuclear units stacking in columns along the two-fold *c* axis (see Figure 3), with interdimer metal–metal distances of 3.497 (Ni) and 3.297 Å (Pd). Each metal atom has five neighbours: four sulphur atoms, which form a square-planar arrangement, and the other metal atom at a distance comparable with that found in the metallic state. The geometry of the nickel and palladium atoms must be regarded as a tetragonally distorted square pyramid, with a metal–metal bond. The following considerations support this interpretation.

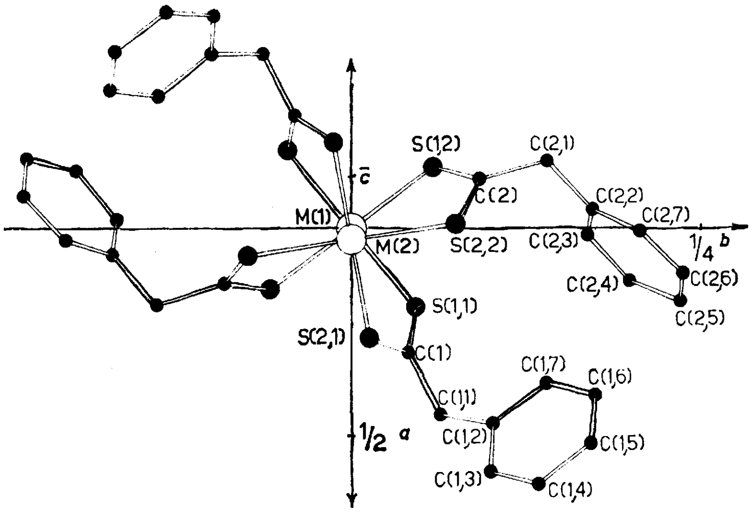

FIGURE 1 Projection of the [$M_2(S_2CCH_2Ph)_4$] molecule (M = Ni or Pd) on the (10$\bar{4}$) plane

TABLE 3

Bond distances (Å) and angles (°), with standard deviations in parentheses, for the nickel complex

(*a*) Distances

Ni(1)–Ni(2)	2.551(3)	C(2,1)–C(2,2)	1.51(2)
Ni(1)–S(1,1)	2.211(5)	C(1,2)–C(1,3)	1.37(2)
Ni(1)–S(1,2)	2.208(6)	C(1,3)–C(1,4)	1.42(3)
Ni(2)–S(2,1)	2.208(3)	C(1,4)–C(1,5)	1.35(3)
Ni(2)–S(2,2)	2.230(7)	C(1,5)–C(1,6)	1.38(2)
S(1,1)–C(1)	1.64(1)	C(1,6)–C(1,7)	1.40(2)
S(1,2)–C(2)	1.65(1)	C(2,2)–C(2,3)	1.40(2)
S(2,1)–C(1)	1.72(1)	C(2,3)–C(2,4)	1.37(2)
S(2,2)–C(2)	1.72(1)	C(2,4)–C(2,5)	1.38(3)
C(1)–C(1,1)	1.52(2)	C(2,5)–C(2,6)	1.38(3)
C(2)–C(2,1)	1.50(2)	C(2,6)–C(2,7)	1.39(2)
C(1,1)–C(1,2)	1.52(2)		

(*b*) Angles

Ni(2)–Ni(1)–S(1,1)	92.6(2)	C(1,1)–C(1,2)–C(1,7)	119(1)
Ni(2)–Ni(1)–S(1,2)	93.4(2)	C(2,1)–C(2,2)–C(2,3)	123(1)
S(1,1)–Ni(1)–S(1,2)	89.9(2)	C(2,1)–C(2,2)–C(2,7)	122(1)
Ni(1)–Ni(2)–S(2,1)	93.9(1)	C(1,3)–C(1,2)–C(1,7)	118(1)
Ni(1)–Ni(2)–S(2,2)	92.8(2)	C(1,2)–C(1,3)–C(1,4)	120(1)
S(2,1)–Ni(2)–S(2,2)	89.3(2)	C(1,3)–C(1,4)–C(1,5)	120(2)
Ni(1)–S(1,1)–C(1)	109.3(4)	C(1,4)–C(1,5)–C(1,6)	121(2)
Ni(1)–S(1,2)–C(2)	108.5(4)	C(1,5)–C(1,6)–C(1,7)	119(1)
Ni(2)–S(2,1)–C(1)	106.9(4)	C(1,6)–C(1,7)–C(1,2)	121(1)
Ni(2)–S(2,2)–C(2)	108.2(4)	C(2,3)–C(2,2)–C(2,7)	115(1)
S(1,1)–C(1)–S(2,1)	126.5(7)	C(2,2)–C(2,3)–C(2,4)	123(2)
S(1,2)–C(2)–S(2,2)	125.5(7)	C(2,3)–C(2,4)–C(2,5)	120(2)
C(1)–C(1,1)–C(1,2)	114(1)	C(2,4)–C(2,5)–C(2,6)	120(2)
C(2)–C(2,1)–C(2,2)	112(1)	C(2,5)–C(2,6)–C(2,7)	119(2)
C(1,1)–C(1,2)–C(1,3)	122(1)	C(2,6)–C(2,7)–C(2,2)	123(1)

(*i*) The two nickel atoms are displaced from the sulphur planes by 0.13 Å to approach each other at a distance of 2.56 Å (*cf.* 2.492 Å in metallic Ni). Displacement of the palladium atoms from the sulphur planes is geometrically less evident (0.06 Å) because of the larger covalent radius, but the Pd–Pd interaction is indeed stronger than the Ni–Ni, the distance of 2.715 Å being shorter than that found in palladium metal (2.751 Å). This stronger tendency of palladium to give a metal–metal bond is confirmed by the structure of bis(ethylene-

TABLE 4

Bond distances (Å) and angles (°), with standard deviations in parentheses, for the palladium complex

(*a*) Distances

Pd(1)–Pd(2)	2.715(3)	C(2,1)–C(2,2)	1.52(2)
Pd(1)–S(1,1)	2.324(5)	C(1,2)–C(1,3)	1.36(2)
Pd(1)–S(1,2)	2.335(5)	C(1,3)–C(1,4)	1.36(2)
Pd(2)–S(2,1)	2.323(6)	C(1,4)–C(1,5)	1.40(2)
Pd(2)–S(2,2)	2.345(6)	C(1,5)–C(1,6)	1.41(2)
S(1,1)–C(1)	1.67(1)	C(1,6)–C(1,7)	1.39(2)
S(1,2)–C(2)	1.68(1)	C(2,2)–C(2,3)	1.41(2)
S(2,1)–C(1)	1.67(1)	C(2,3)–C(2,4)	1.43(2)
S(2,2)–C(2)	1.65(1)	C(2,4)–C(2,5)	1.32(2)
C(1)–C(1,1)	1.53(2)	C(2,5)–C(2,6)	1.39(2)
C(2)–C(2,1)	1.54(2)	C(2,6)–C(2,7)	1.37(2)
C(1,1)–C(1,2)	1.51(2)		

(*b*) Angles

Pd(2)–Pd(1)–S(1,1)	90.6(2)	C(1,1)–C(1,2)–C(1,7)	120(1)
Pd(2)–Pd(1)–S(1,2)	91.4(2)	C(2,1)–C(2,2)–C(2,3)	118(1)
S(1,1)–Pd(1)–S(1,2)	89.9(2)	C(2,1)–C(2,2)–C(2,7)	124(1)
Pd(1)–Pd(2)–S(2,1)	92.7(2)	C(1,3)–C(1,2)–C(1,7)	118(1)
Pd(1)–Pd(2)–S(2,2)	91.6(2)	C(1,2)–C(1,3)–C(1,4)	122(1)
S(2,1)–Pd(2)–S(2,2)	88.9(2)	C(1.3)–C(1,4)–C(1,5)	121(2)
Pd(1)–S(1,1)–C(1)	110.3(4)	C(1,4)–C(1,5)–C(1,6)	118(2)
Pd(1)–S(1,2)–C(2)	108.3(4)	C(1,5)–C(1,6)–C(1,7)	120(1)
Pd(2)–S(2,1)–C(1)	107.8(4)	C(1,6)–C(1,7)–C(1,2)	121(1)
Pd(2)–S(2,2)–C(2)	108.7(4)	C(2,3)–C(2,2)–C(2,7)	118(1)
S(1,1)–C(1)–S(2,1)	129.5(7)	C(2,2)–C(2,3)–C(2,4)	119(1)
S(1,2)–C(2)–S(2,2)	130.3(7)	C(2,3)–C(2,4)–C(2,5)	122(1)
C(1)–C(1,1)–C(1,2)	113(1)	C(2,4)–C(2,5)–C(2,6)	120(2)
C(2)–C(2,1)–C(2,2)	111(1)	C(2,5)–C(2,6)–C(2,7)	120(2)
C(1,1)–C(1,2)–C(1,3)	122(1)	C(2,6)–C(2,7)–C(2,2)	122(2)

1,2-dithiolato)palladium, $[\{Pd(S_2C_2H_2)_2\}_2]$. In this complex, which is dimeric with a direct metal–metal bond, an 'inward distortion' of Pd atoms is again present, whilst the analogous dimeric $[\{Ni(S_2C_2H_2)_2\}_2]$ contains only metal–sulphur interactions in a laterally displaced structure.[7,8]

(*ii*) The two MS_4 units are rotated by *ca.* 26° from the eclipsed structure. Given that the S • • • S 'bite' distance remains constant, an eclipsed structure would have led to an interplanar distance of 3.06 Å. It seems reasonable to suppose that this staggered configuration, with a decreased distance of 2.80 Å between the planes, is determined by the metal–metal bond.

(*iii*) Although the metal–sulphur bond distances of 2.208—2.230(5) Å in $[Ni_2(S_2CCH_2Ph)_4]$ and 2.324—2.345(6) Å in $[Pd_2(S_2CCH_2Ph)_4]$ are similar to those found in the corresponding dithiobenzoates [2.221—2.229(5) and 2.322—2.343(3) Å respectively], such a comparison cannot be made because of the different state of hybridization of the sulphur atoms in these two types of dithiocarboxylates.

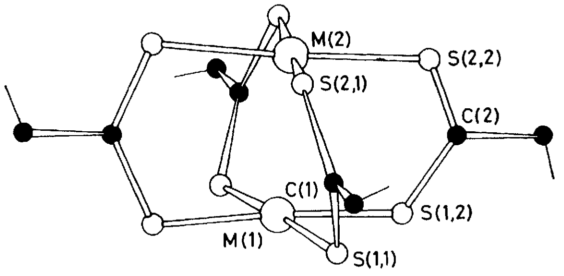

FIGURE 2 Partial 'side' view of the dimeric unit

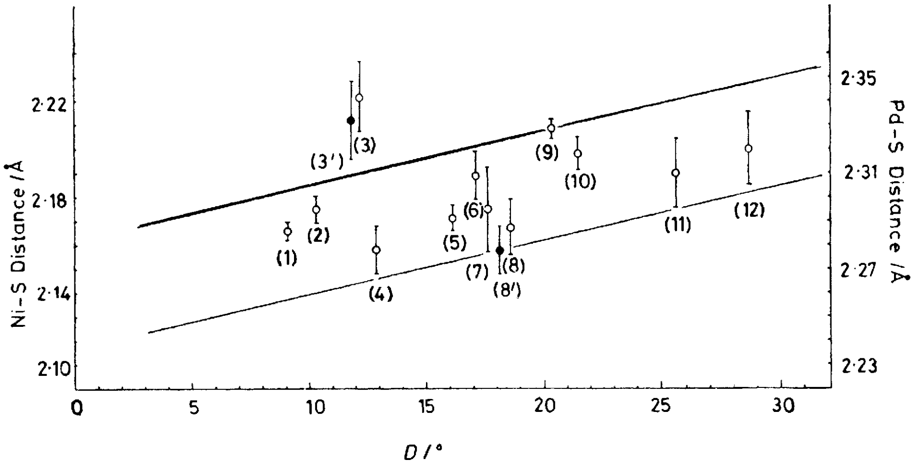

FIGURE 4 Plot of Pd–S (●) and Ni–S (○) bond distances against D values in Table 5. M–S values are accurate to three standard deviations

Thus, in dithiobenzoates the values for the M–S–C and S–M–S angles strongly suggest pure sulphur p bonding,[9] while in phenyldithioacetates it is clear that the sulphur atom uses an sp^2 electron lone pair to form the metal–sulphur σ bond. These metal–sulphur distances must therefore be compared (see Table 5) with those found in nickel and palladium complexes containing sp^2-hybridized sulphur, with comparable –S– and –M– angles. In Table 5 we report M–S distances, –S– and –M– angles, and D, which is a measure of the distortion from the ideal geometry of a square-planar complex with sp^2 sulphur, in which the –S– and –M– angles should be 120 and 90° respectively, *i.e.* $D(°) = |(\text{–S–})° - 120°| + |(\text{–M–})° - 90°|$. It is to be noted that, while complexes (1) and (2) belong, according to Schrauzer,[10] to the class of complexes with 'odd' ligands, in which, as in $[Ni_2(S_2CCH_2Ph)_4]$, metal–ligand π-bonding ability is poor, (4), (5), *etc.* have 'even' ligands with a large extent of π bonding.

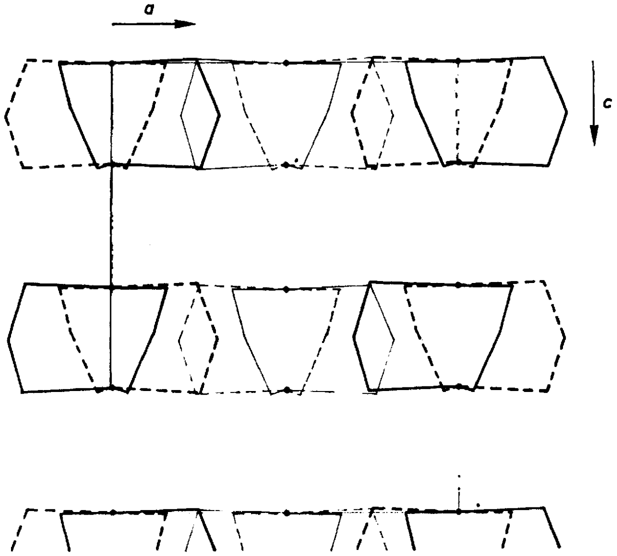

FIGURE 3 (010) Projection of the contents of the unit cell

Figure 4, which gives plots of Ni–S and Pd–S distances

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against D for the complexes of Table 5, shows that: (*a*) the mean value of the Ni–S range increases with the distortion D; (*b*) the differences in the π-bonding abilities of ' odd ' and ' even ' ligands with comparable D values cause only small differences in the Ni–S distances; and (*c*) the mean Ni–S distance (2.212 Å) in $[Ni_2(S_2CCH_2Ph)_4]$ is significantly longer than the expected value (2.16 ± 0.02 Å), in agreement with a strong influence of the metal–metal interaction on the nickel orbitals involved in bonding.

TABLE 5

Principal mean distances (Å), with estimated standard deviations in parentheses, and angles (°), in nickel(II) and palladium(II) square-planar complexes, $[ML_2]$ or $[ML_2]^{2-}$ with anionic ligands containing sp^2-hybridized sulphur atoms in the *trans* configuration. The distortion D(°) is defined in the text

	Angle (°)			
Complex	Ni–S–C	S–Ni–X	D (°)	Ni–S distance (Å)
$[Ni(S_2C_5H_7)_2]$ (1) [a]	118.1	97.2	9.1	2.156(1)
$[Ni(S_2C_2N_3H_4)_2]$ (2) [b]	115.8	96.1	10.3	2.165(2)
$[Ni_2(S_2CCH_2Ph)_4]$ (3) [c]	108.2	89.6	12.2	2.212(5)
$[Ni(S_2C_7H_5)_2]$ (4) [d]	107.3	90.1	12.8	2.148(3)
$[Ni(S_3CPh)_2]$ (5) [e]	108.5	94.6	16.1	2.162(2)
$[Ni(S_2C_2O_2)_2]^{2-}$ (6) [f]	105.8	92.9	17.1	2.179(3)
$[Ni\{S_2C_2(CN)_2\}_2]^{2-}$ (7) [g]	103.9	91.5	17.6	2.165(6)
$[Ni\{S_2C_2(CF_3)_2\}_2]^{2-}$ (8) [h]	102.9	91.5	18.6	2.158(4)
$[Ni(SCH_2CH_2NMe_2)_2]$ (9) [i]	100.8	87.9	20.3	2.198(1)
$[Ni(SCOCH_2NH_2)_2]$ (10) [j]	100.3	88.2	21.5	2.188(2)
$[Ni\{SCMe(NO)\}_2]$ (11) [k]	95.0	89.4	25.6	2.180(5)
$[Ni(NPh{=}N{-}CS{-}N{-}NHPh)_2]$ (12)[l]	95.1	86.3	28.6	2.190(5)
	Pd–S–C	S–Pd–C		Pd–S
$[Pd_2(S_2CCH_2Ph)_4]$ (3′) [c]	108.8	89.4	11.8	2.332(6)
$[Pd(S_2C_2Ph_2)_2]$ (8′) [m]	103.8	87.6	18.6	2.278(3)

[a] $S_2C_5H_7$ = Pentane-2,4-dithionate; R. Beckett and B. F. Hoskins, *J.C.S. Dalton*, 1974, 622. [b] $S_2C_2N_3H_4$ = Biuret anion; H. Luth, E. A. Hall, W. A. Spofford, and E. L. Amma, *Chem. Comm.*, 1969, 520. [c] Present work. [d] $S_2C_7H_5$ = Cyclohepta-2,4,6-triene-1,2-dithionate; G. P. Khare, A. J. Schultz, and R. Eisenberg, *J. Amer. Chem. Soc.*, 1971, **93**, 3597. [e] Ref. 8. [f] D. Coucouvanis, N. C. Baenzinger, and S. M. Johnson, *J. Amer. Chem. Soc.*, 1973, **95**, 3875. [g] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 605. [h] Adduct with norbornadiene; M. Wing, G. C. Tustin, and W. H. Okamura, *J. Amer. Chem. Soc.*, 1970, **92**, 1935. [i] R. L. Girling and E. L. Amma, *Inorg. Chem.*, 1967, **6**, 2009. [j] J. R. Ruble and K. Seff, *Acta Cryst.*, 1972, **B28**, 1272. [k] T. Sato, K. Nagata, Y. Tsukuda, M. Shiro, and H. Koyama, *Chem. Comm.*, 1966, 192. [l] M. Laing, P. Sommerville, and P. A. Alsop, *J. Chem Soc. (A)*, 1971, 1247. [m] Adduct with cyclohexa-1,3-diene; G. R. Clark, J. M. Waters, and R. Whittle, *J.C.S. Dalton*, 1973, 821.

The corresponding values for the few palladium(II) complexes with comparable co-ordination features were superimposed on the plot for nickel, but shifting the y scale by 0.13 Å, the difference between the covalent metal radii (see Figure 4). The coincidence of the positions for complexes (3′) and (3), $[M_2(S_2CCH_2Ph)_4]$ (M = Pd and Ni respectively), and (8′) $[Pd(S_2C_2Ph_2)_2]\cdot C_6H_8$ and (8) $[Ni\{S_2C_2(CF_3)_2\}_2]^{2-}$ is noteworthy. It seems reasonable to conclude that in $[Pd_2(S_2CCH_2Ph)_4]$ the mean Pd–S distance (2.332 Å) is again significantly longer than the expected value (2.29 ± 0.02 Å).

In a recent review, Fackler reported [11] several examples of stacked planar complexes, in which M–M interactions are described according to the Rundle and Cotton–Harris models. Tetrakis(phenyldithioacetato)dipalladium(II) is another example of multinuclear d^8 metal complexes with a metal–metal bond.

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[11] J. P. Fackler, jun., *Progr. Inorg. Chem.*, 1976, **21**, 55 and refs. therein.